

09/719141  
533 Rec'd PCT/PTO 08 DEC 2000

**APPLICATION FOR  
UNITED STATES LETTERS PATENT**

**APPLICANTS:      NOVIS, Yvan  
                      DEPAUW, Jean-Michel  
                      DECROUPET, Daniel**

**INVENTION:**

**TRANSPARENT SUBSTRATE COATED WITH A SILVER LAYER**

This is the entry into the United States National Stage of International Application  
No. PCT/BE99/00071

Jerold I. Schneider  
Arter & Hadden, LLP  
1801 K Street, N.W.  
Suite 400 K  
Washington, D.C. 20006  
202-775-7100  
*Attorneys for Applicants*

Transparent substrate coated with a silver layer

*me*  
*as* →

This invention relates to a transparent substrate, in particular to a coated transparent sheet capable of withstanding heat treatment of a tempering or bending nature without degradation of the coating and adapted for example to be incorporated in a multiple glazing or a laminated glazing.

Many of the terms used to describe the properties of a coated substrate have precise meanings defined in relevant standards. The terms used in this description include the following, most of which are defined by the "Commission Internationale de l'Eclairage" (CIE).

In the present description, two standard illuminants are used: Illuminant C and Illuminant A, as defined by the CIE. Illuminant C represents average daytime light at a color temperature of 6700K. Illuminant A represents the radiation of a Planck radiator at a temperature of about 2856K. This Illuminant represents light emitted by car headlights and is particularly used in evaluating optical properties of vehicle glazings.

The term "luminous transmission" (LTA) as used herein is as defined by the CIE, that is the luminous flux transmitted through a substrate as a percentage of the incident luminous flux for Illuminant A.

The term "energetic transmission" (ET) as used herein is as defined by the CIE, that is the total energy directly transmitted through the substrate without a change in wavelength. It excludes the energy absorbed by the substrate (EA).

The term "color purity" (P) used herein refers to the excitation purity measured with Illuminant C as defined in the Vocabulaire International de l'Eclairage of the CIE, 1987, page 87 and 89. The purity is defined according to a linear scale in which a defined source of white light has a purity of zero and a pure color has a purity of 100%.

For vehicle windows the purity of the substrate is measured from the external face of the window.

The term "dominant wavelength" ( $\lambda_d$ ) used herein designates the wavelength of the peak in a range of wavelengths which are transmitted or reflected by the coated substrate.

The term "non-absorbent material" as used herein designates a material having a refractive index  $[n(\lambda)]$  which is greater than its extinction coefficient  $[k(\lambda)]$  over the whole of the visible spectrum (280 to 780 nm).

The term "emissivity" as used herein designates the normal emissivity of a substrate as defined in the Vocabulaire International de l'Eclairage of the CIE.

The term "haze" as used herein designates the percentage of diffused light transmitted by a material measured according to the ASTM D 1003 standard.

The Hunter coordinates L,a,b used herein measure the coloration of a material as perceived by an observer. They are defined and measured according to the ASTM D 2244 standard.

It has become more and more usual to apply a number of coating layers forming a coating stack to glass sheets to modify their transmission and reflection properties. Previous proposals for metal coating layers and dielectric coating layers in numerous different combinations have been made to confer chosen optical and energetic properties on glass.

Automotive glazings, in particular, are taking increasingly complex forms which require the glass of which they are made to withstand a bending heat treatment operation. In the architectural field it is also increasingly desired for glazings to have curved forms or for the sheets of glass from which they are made to have undergone thermal tempering for shock resistance and thus safety. However, the majority of

coatings intended to be deposited on sheets of glass, particularly those deposited under vacuum, are not able to resist such heat treatment in a satisfactory manner. In particular, their optical properties are significantly degraded during such processes. Thus, it is necessary to apply the coating layers to the sheets of glass after the sheets of glass have taken their final shape or after they have undergone heat treatment which necessitates, particularly for curved glass, particularly complex deposition equipment. Such equipment must enable the deposition of uniform coatings on non-planar substrates.

It has been suggested to overcome this disadvantage by using coating stacks which incorporate coating layers comprised of materials which, when the substrate is raised to the temperature necessary for a tempering or bending heat treatment, can prevent the degradation of the optical properties of the coating stack for the duration of the heat treatment.

This degradation may in particular be attributed to, on the one hand, diffusion of oxygen from the atmosphere or from the dielectric coating layers of the coating stack which leads to oxidation of the metallic layers of the coating stack, and on the other hand to diffusion of sodium from the glass substrate into the coating layers of the coating stack.

European Patent Application No. 761618 describes a method of sputter depositing coatings on a glass substrate according to which the functional metal coating or coatings are surrounded by protecting layers comprising materials adapted to fix the oxygen by oxidation, in particular niobium. According to this document, the absence of degradation of the metallic layers is also due to deposition of the silver layer in a reactive atmosphere comprising at least 10% oxygen.

European Patent Application No. 336257 describes a glass substrate coated with a coating stack which can resist heat treatment and which comprises two metallic coating layers deposited alternatively with three zinc stannate based dielectric coating layers. The first metallic layer is surrounded by titanium protecting layers and the second

metallic layer is overlaid with a protection layer which is also of titanium. This material protects the metallic coating layers during heat treatment by being oxidized itself by combination with the oxygen atoms diffused in the coating stack.

European Patent Application No. 303109 describes a glass substrate coated with a coating stack comprising a silver coating layer surrounded by two coating layers of combination of nickel and chromium which are themselves surrounded by two coating layers of a particular metal oxide. This product is intended to undergo bending by heat treatment in an oxidizing atmosphere during which its luminous transmittance increases significantly.

United States Patent No. 5584902 describes a method of sputter depositing a coating stack capable of withstanding a bending or tempering type of heat treatment on to a glass substrate and which comprises a silver coating layer surrounded by two coating layers of a combination of nickel and chromium which are themselves surrounded by two coating layers of a silicon nitride.

Coating stacks such as suggested by these documents comprise protecting coating layers for the functional coating layers which before a bending or tempering type of heat treatment consist of non-oxidized metal. These protecting coating layers will be oxidized during heat treatment such that the optical properties of the coated substrate will be significantly modified during this process. In addition, it is necessary that these protecting coating layers are not oxidized to their interface with the functional metal layers so that the functional metallic layers are not subjected to oxidation. This is unfavorable for obtaining a high luminous transmission of the finished product.

### SUMMARY OF THE INVENTION

The present invention relates to a transparent substrate carrying a coating stack comprising at least one metallic coating layer comprising silver or a silver alloy, each metallic coating layer being in contact with two non absorbent transparent dielectric coating layers, the coated substrate being adapted to withstand a bending or tempering type of heat treatment, characterized in that prior to such heat treatment, each of the

dielectric coating layers comprises a sub-layer based on a partially oxidized combination of two metals.

5 We have surprisingly discovered that the presence prior to heat treatment  
 of sub-layers based on a partially oxidized combination of two metals in the coating stack  
 in accordance with the invention protects each metallic coating layer of the coating stack  
 and that this enables a product that withstands this treatment particularly well to be  
 obtained. We have also noted that the luminous transmittance of the substrate at the end  
 of the said heat treatment is higher than when metallic protecting coatings layers are used.  
 As the sub-layers based on a combination of two metals according to the invention are not  
 10 totally oxidized before heat treatment they allow the absorption of the diffused oxygen in  
 the coating stack during this treatment and thus protect the metallic coating layers from  
 oxidation. In addition, by arranging for these sub-layers to be partially oxidized across  
 their entire thickness before heat treatment, the luminous transmission of the product after  
 heat treatment is greater than if the sub-layers were, prior to heat treatment, non-oxidized  
 15 sub-layers of the same combination of metals. Furthermore, the structure of protecting  
 sub-layers which are partially oxidized during deposition is more favorable to the optical  
 properties of the finished product than when these sub-layers are only oxidized during a  
 heat treatment following deposition of the coating stack.

20 Preferably, the sub-layers based on a combination of two metals comprise  
 Ni and Cr. This combination once oxidized during deposition and heat treatment has a  
 greater transparency ~~that~~ that of sub-layers based on combinations of other metals. In  
 addition, use of a combination of Ni and Cr in combination with the different coating  
 layers of the coating stack allows the finished product to display advantageous optical  
 properties.

25 According to one preferred form of the invention, at least the sub-layer  
 based on a combination of two metals which is the furthest spaced from the substrate is  
overlaid with a sub-layer comprising a nitride, preferable a nitride of Si, of Al or of a  
 combination of these elements. Such materials act as barriers to oxygen diffusion in the

coating stack and thus limit the quantity of oxygen which arrives at the underlying sub-layer based on a combination of two metals. This is advantageous in allowing heat treatment in very oxidizing conditions without necessitating increases in the thickness of the sub-layers based on a combination of two metals. By overlaying the said sub-layer based on a combination of two metals with a sub-layer of a nitride compound, the sub-layer covered in this way is always able to absorb the entire amount of oxygen which reaches it and thus to maintain its protecting effect with respect to the underlying metallic coating layer.

In one preferred form of the invention at least one metallic coating layer is in contact with an underlying sub-layer comprising an oxide of a metal chosen, in particular, from Ti, Ta, Nb, and Sn. These metals have a crystalline structure which favors recrystallisation of the Ag during heat treatment in such a way that substantially no visible haze appears in the finished product. This is advantageous as when a coating stack comprising a metallic coating layer undergoes a tempering or bending type of heat treatment, the crystalline structure of this coating layer undergoes modifications which can appear macroscopically by the appearance of haze in the coating stack visible in the finished product. Such haze is considered inaesthetic.

Advantageously, at least the sub-layer based on a combination of two metals which is closest to the substrate is in contact with an underlying sub-layer of an oxide of Ti. This is advantageous as the optical properties of a coating stack destined to withstand a tempering or bending type of heat treatment may be deteriorated by diffusion in the lower coating layers of the coating stack of sodium migrating from the upper layers of the glass substrate. An oxide of Ti has inherent properties to block such migration.

Preferably, the dielectric coating layer in contact with the substrate comprises sub-layers of oxides of metals or combinations of metals. As this coating layer is the furthest spaced from the main source of diffusing oxygen, that is the atmosphere, it is not strictly necessary that it comprises a sub-layer of a nitride adapted to block such oxygen diffusion.

In another preferred form of the invention, each metallic coating layer of the coating stack comprises a combination of Ag and Pt or Pd. The addition of one of these elements to the silver confers upon the coating stack a better resistance to corrosion due to ambient humidity.

5           The coating layers of the coating stack may be completed by a thin final coating layer which provides the coating stack with improved chemical and/or mechanical durability without significantly altering its optical properties. Oxides, nitrides and oxynitrides of silicon, aluminum or combinations of these elements may provide this effect. Silica ( $\text{SiO}_2$ ) is generally preferred.

10           When the coating stack according to the invention has a single metallic coating layer, the optical thickness of the dielectric coating layer closest to the substrate is preferably between 50 and 90 nm, that of the other dielectric coating layer is preferable between 70 and 110 nm, that of the sub-layers based on a combination of two metals is preferably between 3 and 24 nm and the geometrical thickness of the metallic coating  
15   layer is preferably between 8 and 15 nm. These ranges of thicknesses allow a coated substrate to be obtained which, after a tempering or bending type of heat treatment has a haze of less than 0.3%.

Such a coating stack deposited on a 4mm thick clear sodalime glass substrate preferably confers to the substrate after a tempering or bending type of heat  
20   treatment a LT greater than 77%, an emissivity less than 0.08 and preferably less than 0.05, a dominant wavelength in reflection of 450 to 500 nm, more preferably from 470 to 500 nm, and a color purity in reflection of 5 to 15%.

Preferably, the thicknesses of the coating layers and sub-layers of a coating stack according to the invention having a single metallic coating layer are chosen between  
25   the preferred thicknesses such that during heat treatment, the variation in LTA of the coated substrate is less than 10%, the variation of the dominant wavelength in reflection



does not exceed 3 nm and the variation in the color purity in reflection does not exceed 5%.

Such a product may be used in the manufacture of so called low emissivity multiple glazings for buildings. In this case, it is associated with at least one transparent sheet of vitreous material from which it is separated by a volume of gas and has its boundaries limited by a peripheral spacer. In such a glazing, the coated surface is directed towards the gas filled space. In the case of architectural use of a product in accordance with the invention, the coating stack may only have a single metallic coating layer.

It is remarkable that the emissivity after heat treatment of substrates coated according to the invention is of the same order of magnitude as that of standard low emissivity glazings, that is to say those which have not withstood heat treatment, which is generally less than 0.10 in the case of coating stacks deposited by sputtering for LTA of the order of 80%. Multiple glazings incorporating a sheet of glass coated according to the invention and having undergone a tempering or bending type of heat treatment thus offer equivalent optical properties to those of a glazing comprising a sheet of coated glass which has not undergone heat treatment whilst providing, when the coated substrate is tempered, a better mechanical shock resistance and improved safety to the occupants of areas in which these glazings are installed.

When a coating stack in accordance with the invention comprises two metallic coating layers, the optical thickness of the dielectric coating layer closest to the substrate is preferably between 50 and 80 nm, that of the dielectric coating layer spaced furthest from the substrate is preferably between 40 and 70 nm, that of the intermediate dielectric coating layer is preferably between 130 and 170 nm, that of the sub-layers based on a composition of two metals is preferably between 3 and 24 nm and the geometrical thickness of the metallic coating layers is preferably between 8 and 15 nm.

Such a coating stack deposited on a clear 2.1mm thick sodalime glass substrate confers on the substrate, after a tempering or bending type heat treatment, a haze

of less than 0.5%, a LTA of greater than 76%, a dominant wavelength in reflection between 450 and 500nm, preferably between 470 and 500nm, and a color purity in reflection between 5 and 15%.

Such a product may be used to form part of a multiple glazing. It may also be advantageously used as part of a laminated glazing, particularly a vehicle windshield. Legal requirements for windshields require a luminous transmission (LTA) of at least 70% in the USA and at least 75% in Europe. With respect to solar energy, the total energy directly transmitted (ET) is preferably less than 50%. A further factor is the color of the coated substrate which must satisfy the requirements of the automotive industry. These requirements generally necessitate that a coating stack according to the invention which is applied to a sheet of glass of a laminated glazing intended to form a vehicle windshield comprises at least two metallic coating layers. When the coated substrate is used in such a structure, it may be useful to employ a thin final coating layer as described above to reduce the risk of delamination of the laminated glazing.

The metallic coating layers of a coating stack in accordance with the invention may be connected to a source of electrical current such that they give off heat by the Joule effect. Such a windshield may thus be de-iced or de-misted.

The invention also relates to a method of manufacture of a product such as described above using a sputtering deposition technique to deposit coating layers of the coating stack.

Preferably, each metallic coating layer is deposited in an oxidizing atmosphere, in particular comprising argon and oxygen. In particularly preferred forms of the invention, the atmosphere in which each metallic coating layer is deposited comprises less than 10% and preferably between 3 and 7% oxygen. These concentrations allow better thermal stability of these coating layers when compared with identical coating layers deposited in an inert atmosphere whilst being of a sufficiently low concentration to avoid any risk of oxidation of the metal during its deposition.

The materials which comprise the dielectric layers, with the exception of the sub-layers based on a composition of two metals, are preferably deposited from cathodes having an alternating current supply. This process has the advantage of producing coating layers with a density and structure which is more effective in resisting diffusion of sodium and oxygen in the coating stack during a tempering or bending type heat treatment than when cathodes having a direct current supply are used to deposit the same coating layers. Nevertheless, the advantage in terms of density and structure of the coating layers is only obtained by this process for thicknesses of coating layers which are greater than those of the sub-layers based on a composition of two metals. For this reason, these sub-layers based on a composition of two metals are not deposited by this method.

The invention will now be described in greater detail with reference to the following non-limitative examples.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

### EXAMPLES

Two types of clear sodalime sheet glass substrate samples of 2.1mm and 4 mm thick are passed through in-line deposition equipment comprising five vacuum enclosures (at a pressure of 0.3 Pa), a substrate conveyor, power sources and gas admission valves. Each depositing enclosure contains magnetron assisted sputtering cathodes, gas entries and evacuation outlets, the deposition being obtaining by moving the substrate a number of times under the cathode.

The first enclosure contains two cathodes provided with targets formed from titanium. These cathodes are supplied from an alternating current source to which they are connected such that each works alternatively according to the frequency of the current to deposit a first coating layer of an oxide of Ti in an atmosphere of oxygen and argon. The second enclosure contains a cathode which is a combination of Ni and Cr

supplied by a direct current source to deposit a non-absorbent partially oxidized sub-layer of a combination of Ni and Cr in an atmosphere of oxygen and argon. The third enclosure is the same as the first enclosure to deposit a third sub-layer of an oxide of Ti. The fourth enclosure is subdivided into two compartments. The first of these contains a cathode of Ag supplied from a direct current source to deposit a coating layer of metallic Ag in an atmosphere of argon and oxygen, and the second contains a cathode of a combination of Ni and Cr supplied by a direct current source to deposit a non-absorbent partially oxidized sub-layer of a combination of Ni and Cr in an atmosphere of oxygen and argon which is more oxidizing than the first enclosure. The fifth enclosure contains two silicon cathodes supplied from an alternating current source to deposit a non-absorbent sub-layer of silicon nitride in a nitrogen atmosphere. This sequence of enclosures is repeated for the deposition of a coating stack comprising two metallic coating layers.

Table A sets out the optical and energetic properties of coated substrates intended for use as part of a multiple glazing both before heat treatment (the numbers <sup>without</sup> ~~with~~ apostrophes) and after heat treatment. The thicknesses given are in nm.

In this case, the following sequence is deposited on a 4mm thick clear sodalime glass substrate:

a non-absorbent sub-layer of an oxide of titanium,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ratio of 80/20,

a non-absorbent sub-layer of an oxide of titanium,

a coating layer of silver,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ratio of 80/20,

a sub-layer of silicon nitride.

The coated substrate subsequently undergoes a tempering heat treatment with a 3 min pre-heating at 570° C followed by a 3 min tempering heating at 700° C.

Table B sets out the optical and energetic properties before (A) and after (A') heat treatment of a coated substrate intended for use in a multiple glazing having a coated stack which is not in accordance with the present invention. This coating stack comprises protecting layers for the metallic coating layer which comprise a non-oxidized combination of Ni and Cr. This comparative example shows that such a coating stack has both an emissivity and a haze which is greater than the products according to the invention.

Table C sets out the optical and energetic properties of coated substrates before heat treatment (the numbers with apostrophes) and after heat treatment which are intended for use as part of a laminated glazing. The thicknesses given are in nm.

In this case, the following sequence is deposited on a 2.1 mm thick clear sodalime glass substrate:

a non-absorbent sub-layer of an oxide of titanium,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ratio of 80/20,

a non-absorbent sub-layer of an oxide of titanium,

a coating layer of silver,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ration of 80/20,

a sub-layer of silicon nitride,

a sub-layer of an oxide of titanium,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ratio of 80/20,

5 a coating layer of silver,

a protecting, non-absorbent sub-layer of a partially oxidized combination of nickel and chrome in a weight ration of 80/20,

a sub-layer of silicon nitride.

10 The coated substrate subsequently undergoes a bending heat treatment at a temperature of 635° C during 12 min.

It is then incorporated into a laminated sheet comprising, in order, the said coated substrate, an adhesive sheet of polyvinalbutyral (PVB) having a thickness of 0.76 mm and second sheet of clear 2.1 mm thick sodalime glass. Example 17'' sets out the optical properties of a laminated glazing comprising a coated substrate in accordance with  
15 example 17.

When the coating stacks according to the examples of Table C are intended to be used in multiple glazings for buildings, they are deposited on sodalime glass substrates of 4 or 6 mm thick. The optical properties set out in the said table are the same with the exception of LTA which is reduced by about 0.5% by mm of increased thickness  
20 of the substrate.

TABLE A

| Ex.                                 | 1     | 1'    | 2     | 2'    | 3     | 3'    |
|-------------------------------------|-------|-------|-------|-------|-------|-------|
| TiO <sub>2</sub> (nm)               | 19.0  | 19.0  | 21.5  | 21.5  | 15.5  | 15.5  |
| NiCrOx (nm)                         | 10.0  | 10.0  | 6.0   | 6.0   | 6.0   | 6.0   |
| TiO <sub>2</sub> (nm)               | 0.0   | 0.0   | 0.0   | 0.0   | 6.0   | 6.0   |
| Ag (nm)                             | 13.5  | 13.5  | 14.0  | 14.0  | 14.0  | 14.0  |
| NiCrOx (nm)                         | 3.3   | 3.3   | 3.3   | 3.3   | 3.3   | 3.3   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 50.0  | 50.0  | 50.0  | 50.0  | 50.0  | 50.0  |
| LTA4 (%)                            | 76.5  | 81.4  | 74.7  | 80.2  | 74.1  | 78.1  |
| $\epsilon$                          | 0.050 | 0.050 | 0.050 | 0.040 | 0.050 | 0.030 |
| $\lambda_D$ (nm)                    | 475.2 | 474.2 | 478.7 | 476.4 | 478.1 | 477.6 |
| P (%)                               | 22.1  | 20.2  | 17.7  | 16.3  | 18.1  | 14.1  |
| haze (%)                            | 0.20  | 0.20  | 0.16  | 0.19  | 0.16  | 0.18  |

| Ex.                                 | 4     | 4'    | 5     | 5'    | 6     | 6'    |
|-------------------------------------|-------|-------|-------|-------|-------|-------|
| TiO <sub>2</sub> (nm)               | 17.5  | 17.5  | 17.5  | 17.5  | 11.5  | 11.5  |
| NiCrOx (nm)                         | 7.5   | 7.5   | 7.5   | 7.5   | 6.0   | 6.0   |
| TiO <sub>2</sub> (nm)               | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| Ag (nm)                             | 10.5  | 10.5  | 10.5  | 10.5  | 23.0  | 23.0  |
| NiCrOx (nm)                         | 6.0   | 6.0   | 12.0  | 12.0  | 6.0   | 6.0   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 21.0  | 21.0  | 15.0  | 15.0  | 6.0   | 6.0   |
| LTA4 (%)                            | 79.0  | 81.9  | 78.0  | 78.5  | 80.0  | 82.0  |
| $\epsilon$                          | 0.080 | 0.058 | 0.075 | 0.062 | 0.092 | 0.074 |
| $\lambda_D$ (nm)                    | 477.5 | 471.8 | 479.6 | 478.1 | 497.9 | 482.5 |
| P (%)                               | 15.4  | 10.5  | 15.6  | 9.3   | 6.2   | 34.1  |
| haze (%)                            | 0.10  | 0.18  | 0.10  | 0.17  | 0.16  | 0.29  |

TABLE A (continued)

| Ex.                                 | 7     | 7'    | 8     | 8'    | 9     | 9'    |
|-------------------------------------|-------|-------|-------|-------|-------|-------|
| TiO <sub>2</sub> (nm)               | 23.0  | 23.0  | 23.0  | 23.0  | 13.0  | 13.0  |
| NiCrOx (nm)                         | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| TiO <sub>2</sub> (nm)               | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| Ag (nm)                             | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  |
| NiCrOx (nm)                         | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 50.0  | 50.0  | 21.0  | 21.0  | 21.0  | 21.0  |
| LTA4 (%)                            | 84.0  | 87.4  | 76.0  | 77.1  | 80.0  | 83.1  |
| $\varepsilon$                       | 0.090 | 0.073 | 0.099 | 0.076 | 0.095 | 0.066 |
| $\lambda_D$ (nm)                    | **    | 453.4 | 481.4 | 482.1 | 478.6 | 473.7 |
| P (%)                               | **    | 7.7   | 12.0  | 6.8   | 16.0  | 12.3  |
| haze (%)                            | 0.12  | 0.27  | 0.14  | 0.25  | 0.08  | 0.20  |

TABLE B

| Ex. | SnO2<br>(nm) | NiCr<br>(nm) | Ag<br>(nm) | NiCr<br>(nm) | SnO2<br>(nm) | LTA4<br>(%) | $\varepsilon$ | $\lambda_D$<br>(nm) | P<br>(%) | haze<br>(%) |
|-----|--------------|--------------|------------|--------------|--------------|-------------|---------------|---------------------|----------|-------------|
| A   | 38.0         | 1.2          | 10.5       | 1.2          | 46.0         | 68.0        | 0.090         | 474.5               | 14.5     | 0.20        |
| A'  | 38.0         | 1.2          | 10.5       | 1.2          | 46.0         | 77.5        | 0.130         | 470.0               | 20.0     | 0.40        |

N.B.:  $\lambda_D$  et P are measured in reflection from the coated side



TABLE C

| Ex.                                 | 10    | 10'   | 11    | 11''  | 12    | 12'   | 13    | 13'   |
|-------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| TiO <sub>2</sub> (nm)               | 13.0  | 13.0  | 14.0  | 14.0  | 14.0  | 14.0  | 13.0  | 13.0  |
| NiCrOx (nm)                         | 7.5   | 7.5   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| TiO <sub>2</sub> (nm)               | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   | 6.0   |
| Ag (nm)                             | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  |
| NiCrOx (nm)                         | 3.3   | 3.3   | 1.7   | 1.7   | 1.7   | 1.7   | 1.7   | 1.7   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 44.5  | 44.5  | 46.0  | 46.0  | 47.0  | 47.0  | 51.0  | 51.0  |
| TiO <sub>2</sub> (nm)               | 19.5  | 19.5  | 19.5  | 19.5  | 19.5  | 19.5  | 19.5  | 19.5  |
| NiCrOx (nm)                         | 3.0   | 3.0   | 3.0   | 3.0   | 1.7   | 1.7   | 1.7   | 1.7   |
| TiO <sub>2</sub> (nm)               | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   |
| Ag (nm)                             | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  | 10.5  |
| NiCrOx (nm)                         | 6.0   | 6.0   | 5.0   | 5.0   | 5.0   | 5.0   | 6.0   | 6.0   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 21.0  | 21.0  | 22.0  | 22.0  | 22.0  | 22.0  | 27.0  | 27.0  |
| LTA (%)                             | 71.0  | 76.4  | 71.0  | 77.2  | 72.0  | 78.5  | 72.0  | 78.1  |
| $\lambda_D$ (nm)                    | 498.7 | 484.0 | 516.9 | 487.9 | 497.8 | 485.6 | 475.3 | 540.5 |
| P (%)                               | 1.83  | 13.2  | 2.3   | 11.1  | 3.4   | 13.0  | 13.4  | 4.0   |
| haze (%)                            | 0.11  | 0.48  | 0.14  | 0.46  | 0.12  | 0.48  | 0.10  | 0.45  |

TABLE C (continued)

| Ex.                                 | 14   | 14'   | 15    | 15'   | 16   | 16'   | 17   | 17'   | 17''  |
|-------------------------------------|------|-------|-------|-------|------|-------|------|-------|-------|
| TiO <sub>2</sub> (nm)               | 16.0 | 16.0  | 16.0  | 16.0  | 16.0 | 16.0  | 16.0 | 16.0  | 16.0  |
| NiCrOx (nm)                         | 6.0  | 6.0   | 6.0   | 6.0   | 6.0  | 6.0   | 6.0  | 6.0   | 6.0   |
| TiO <sub>2</sub> (nm)               | 6.0  | 6.0   | 6.0   | 6.0   | 6.0  | 6.0   | 6.0  | 6.0   | 6.0   |
| Ag (nm)                             | 10.5 | 10.5  | 10.5  | 10.5  | 10.5 | 10.5  | 10.5 | 10.5  | 10.5  |
| NiCrOx (nm)                         | 1.7  | 1.7   | 1.7   | 1.7   | 3.2  | 3.2   | 2.5  | 2.5   | 2.5   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 51.0 | 51.0  | 51.0  | 51.0  | 51.0 | 51.0  | 51.0 | 51.0  | 51.0  |
| TiO <sub>2</sub> (nm)               | 19.5 | 19.5  | 19.5  | 19.5  | 19.5 | 19.5  | 19.5 | 19.5  | 19.5  |
| NiCrOx (nm)                         | 2.5  | 2.5   | 2.5   | 2.5   | 2.5  | 2.5   | 2.5  | 2.5   | 2.5   |
| TiO <sub>2</sub> (nm)               | 0.0  | 0.0   | 0.0   | 0.0   | 0.0  | 0.0   | 0.0  | 0.0   | 0.0   |
| Ag (nm)                             | 10.5 | 10.5  | 10.5  | 10.5  | 10.5 | 10.5  | 10.5 | 10.5  | 10.5  |
| NiCrOx (nm)                         | 6.0  | 6.0   | 6.0   | 6.0   | 6.0  | 6.0   | 6.0  | 6.0   | 6.0   |
| Si <sub>3</sub> N <sub>4</sub> (nm) | 32.0 | 32.0  | 27.0  | 27.0  | 27.0 | 27.0  | 27.0 | 27.0  | 27.0  |
| LTA (%)                             | 72.0 | 78.3  | 72.0  | 78.2  | 71.0 | 77.2  | 71.0 | 77.5  | 76.9  |
| ET (%)                              |      |       |       |       |      |       |      |       | 40.8  |
| $\lambda_D$ (nm)                    | **   | 476.8 | 455.7 | 480.0 | **   | 477.9 | **   | 478.3 | 477.6 |
| P (%)                               | **   | 9.6   | 6.1   | 17.3  | **   | 14.7  | **   | 16.2  | 10.7  |
| haze (%)                            | 0.09 | 0.48  | 0.12  | 0.47  | 0.08 | 0.47  | 0.10 | 0.46  | 0.46  |

N.B.:  $\lambda_D$  and P are measured in reflection from the glass side

\*\* : purple nuance for which no precise value of  $\lambda_D$  and P can be determined.